

Elemental Composition of Sized Particles
Emitted from Stationary Sources

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16. ABSTRACT This paper discusses several approaches for obtaining the elemental and, in a few cases, inorganic compound identification in sized particles. The earlier work described is for particles in the size range down to about 0.25 μm which were separated by inertial devices such as impactors and cyclones. Both in-stack and extractive devices were used. A recent development of an in-stack diffusion device that collects sized particles on a filter medium in the size range of 0.01 to 0.4 μm is being used to cover that size range. The elemental analyses are done by wavelength dispersion x-ray fluorescence (WXRF). Fourier Transform infrared is being used for inorganic compound determination. The WXRF technique gives the best results for particles that are uniformly deposited on light weight filter media. The standard impactors do not collect the particles in this manner and, therefore, some sample preparation or transfer is needed. The sample preparation and transfer techniques used in this research are also described. In addition, an in-stack impactor developed to collect the sized particles as a uniform deposit will be discussed. The results of the chemical analyses from sized particles collected from various types of industries will be presented.		
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ELEMENTAL COMPOSITION OF SIZED PARTICLES
EMITTED FROM STATIONARY SOURCES

by

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Abstract

This paper describes several approaches for obtaining the elemental content of sized particles. The main analytical technique used was x-ray fluorescence analyses (XRF). Devices for collecting sized particles are described. A diffusion device was used for particles from 0.01 to 0.4 μm diameters and a special XRF compatible impactor was used for particles of 0.25 μm and larger diameters.

Introduction

The physical and chemical characterization of source-emitted particles is important in several phases of air pollution research. The chemical composition and particle size data are needed for health effects studies, air chemistry research, and air quality modeling. Physical characteristics such as particle size, resistivity, density and refractive indices are used in pollution measurement methods, emission control research, transport and fate studies, and air quality modeling.

The chemical composition of air pollution particulate matter has, in the past, generally, been limited to elemental analyses on total particulate matter. However, some current research projects require knowledge of the chemical composition of sized particles. In some projects, such as acid rain and health effects studies, the inorganic compound content is required. Henry and Knapp [1] have developed techniques to identify and measure certain inorganic compounds. The major tool in this approach is Fourier-Transform Infrared spectroscopy (FTIR). While FTIR only measures covalent bond vibrations such as in the sulfate, nitrate and phosphate ions, enough spectral band shape changes, frequency shifts, and new bands appear from the various cations, crystal phases and waters of hydration that the inorganic compounds can be measured. These measurements included different crystal phases and waters of hydration for many compounds. The FTIR is limited to compounds with some covalent bonds and ionic compounds such as NaCl cannot be measured by FTIR. Because this technique requires removal of the sample from the collecting substrate and dispersing in KBr, generally not enough sized material is available, and therefore, only a limited number of samples have been analyzed by FTIR.

X-ray fluorescence (XRF) spectroscopy is a powerful technique for elemental analyses. XRF is generally fast, nondestructive, and can analyze most elements above atomic number 8 on the collecting filters. A wavelength-dispersive XRF system described by Bennett, Wagman, and Knapp [2] at the U.S. Environmental Protection Agency (EPA) Research Center at Research Triangle Park (RTP), North Carolina can determine 30 elements on filter samples in about 10 minutes per sample, including data processing and printout. The detection limits of this system are given in Table 1.

The major drawback in using XRF on sized particle samples is that, for best results, the particles must be uniformly deposited on a substrate. Most particle-sizing systems such as impactors, cyclones, and diffusion batteries do not collect samples in this manner. Therefore, to determine the elemental content of samples collected with these sizing devices, extensive sample preparation is required. A sample transfer technique has been developed and used at EPA-RTP.

To overcome the nonuniform collection of particle-sizing devices, programs at EPA-RTP were initiated to develop systems that would collect sized particles in uniform deposits compatible with the XRF system. For particles with a size between 0.01 and 0.4 μm diameters, an in-stack diffusion device was developed by Lundgren [3] of the University of Florida on a grant from EPA-RTP. A cascade impactor that collects uniform deposits of sized particles of 0.25 μm diameter and greater in five sized cuts, of 0.5, 1, 2, 4, and 8 μm D_{50} , was developed by Southern Research Institute of Birmingham, Alabama on a contract from EPA-RTP [4]. The system uses a precutter cyclone to remove large particles. Two pre-cutters are available with D_{50} 's of 10 and 15 μm . The precutter and back-up filter provide two more size cuts for a total of 7 cuts. These systems and the transfer techniques are described below.

Methods

Conventional In-Stack Impactors

The conventional in-stack cascade impactors used for source emission particle size distribution measurements collect the sized particles in little piles on a substrate. This type of collection is due to the impactor design, with most in-stack impactors having a number of small round holes or rectangular slits to accelerate the particles. The sized particle collections are made on some substrate located under these acceleration jets. After collection, the substrates are removed and weighed and the particle size distribution determined. If chemical analyses are required, further sample preparation is needed.

Attempts were made to transfer the sized particles from the substrates to a filter by suspending the particles in a nonpolar organic solvent and then filtering. However, with all the solvents tried, sufficient amounts

of key elements such as S, V, and Cd were lost because of their solubilities in these solvents; this approach was, therefore, abandoned. A transfer technique was developed with minimum losses. In this technique the particles are suspended in a volatile solvent, such as methylene chloride or pentane, then quantitatively transferred to a specially designed system with a glass or plastic cylinder held over the desired substrate. The solvent is evaporated under nitrogen or dry air. The cylinder wall is carefully washed down periodically during solvent evaporations to prevent wall losses. A uniform deposit of the particles on the substrate is obtained which is then analyzed by XRF. However, the transfer step is tedious and time consuming and since the impactor used has seven stages, seven transfers are required. A blank is always carried through the procedure.

Diffusion Classifier

The in-stack impactors used are limited to a size separation of particles about 0.25 μm diameters or greater. When particles of smaller sizes are to be separated, another approach is needed such as diffusion classifiers or batteries. These devices generally separate particles of 0.01 to about 0.4 μm diameters. In the early use of diffusion batteries, the particles were extracted with a probe from the source and fed into the diffusion batteries. The particles passing through the diffusion batteries were counted with a particle counting system such as a condensation nuclei counter or electrical aerosol analyzer with no particles being collected for further analyses. An in-stack diffusion classifier based on the ambient system of Sinclair and others [5,6] was developed for EPA-RTP by Lundgren. This device measures source emitted aerosols of 0.01 to 0.4 μm diameters. The particles are separated in five stages, each one with a different number of very fine mesh stainless steel wire screens. The five stages operate in parallel, each sampling at the same fixed flow rate. The sampling rates are maintained through each stage by using carefully matched critical orifices.

Four of the five stages contain screens. The numbers in a standard run in the four stages are 5, 10, 20, and 36 identical screens. The fifth stage has no screen and provides a measure of the total aerosol sample. Collection filters are positioned after the screens in each stage.

When the aerosol passes through a set of screens, small particles are deposited on the screens by diffusion and the larger particles pass through and are collected on the after-filter. The amount of collected aerosol is determined by weighing the filter. The efficiency of large particle removal increases with the number of screens resulting in lower mass penetration and smaller filter weight gains. Since these exposed filters have a uniform deposit, they are analyzed by XRF as received.

The calibration of the system agreed well with the theory for particles with diameters between 0.03 μm and 0.2 μm , flow rates of 2, 3, 4 and 5 lpm and temperatures up to 370°C. No particles below 0.03 μm were used. The deviation from theory in particle penetration about 370°C was unexpected, and no explanation has been found. The D_{50} of the four stages with screens at 27°C were 0.2 μm for 36 screens, 0.1 μm for 20 screens, 0.05 μm for 10 screens, and 0.03 μm for 5 screens.

In general, the system works well. However, for best results, a pre-separator to remove the particles with diameters $> 0.4 \mu\text{m}$ is needed. In several studies, impactors or series cyclones have been coupled with the diffusion classifier to give a size range from about 0.01 to $> 20 \mu\text{m}$. Sampling times of 4 to 6 hours are generally required to collect enough material for good size and chemical results.

XRF-Compatible Impactor

To overcome the need to transfer the sized particles to a uniform sample for XRF analyses, an XRF-compatible impactor has been developed. This impactor consists of five impactor stages, a precutter, and a back-up filter. The impactor stages consist of a slit impactor jet with an oscillating drum beneath the jet. This drum collects the sample evenly over a 31 mm x 34 mm area. Special substrates with sticky coating of low XRF background material were developed for collecting the samples. These substrates are removed from the drum after collection and analyzed directly by XRF.

The impactor developed by Southern Research Institute in Birmingham, Alabama is constructed of 316 stainless steel screens and fits through a 4-in (100 mm) sampling port. The D_{50} 's of the five stages are 8, 4, 2, 1, and 0.5 μm . The system can operate effectively up to about 150°C. The details are given in an EPA report by Felix, Hussey, and McCain [4].

Discussion and Results

Standard in-stack impactor runs on emissions from several oil-fired power plants burning high S, high V fuel have been analyzed by the transfer XRF technique. The results for a typical run are given in Table 2. Sulfur is fairly uniformly distributed. The metals in general show a decrease in content as the particle sizes decrease. Both V and Ni show an increase on the back-up filter that should contain the particles below 0.25 μm diameter. The difference in the V could be due to the presence of at least two forms of V as reported by Henry and Knapp [1]. These two forms are V_2O_5 and $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$.

Similar results were found with samples collected with a series of 3 small cyclones at an oil-fired plant operated at different excess O levels. At normal operation, 0.2% excess O, the V is divided almost 50/50 between the largest D_{50} cyclone and the back-up filter. When the excess O is increased to 1%, most of the V is found on the back-up filter. The same holds for S and Ni. These changes are probably due to the burning off of the large soot content in the 0.2% excess O, which tends to absorb the S and V compounds. These results are shown in Table 3.

The diffusion classifier has been used to collect emissions from several industries including oil-fired and coal-fired power plants, jet engine test cells, and municipal waste incinerators. However, only the runs from coal-fired power plants have been analyzed by XRF. Table 4 contains the average results from six runs for the five most prominent elements. The emissions were from a plant burning low, 0.2% S coal. The most surprising results are for Fe, which show a fairly high content for the smallest size fraction, less than 0.03 μm . Five of the six runs had high Fe in this fraction with a range in values from 7 to 47 μg . The mean value for the 5 runs is 23.9 μg with a 15.6 σ . All six runs had high Fe in the largest size range > 0.3 μm with a range of 9 to 77 μg , a mean value of 30 μg with a σ of 25. The Mg and Al content increased with increasing particle size while Si and Ca content was fairly constant.

The first field test of the XRF impactor was at a pulp and paper mill. These results are given in Tables 5 and 6. Table 5 presents the data for main elements determined in two runs on the emissions from a recovery boiler. The high sulfur in the larger fractions was unexpected.

This could be due to the absorption of sulfuric acid on the larger particles. The results in Table 6 are a more complete list of elements in the emissions from another recovery boiler. As expected, the sulfur content increased with decreasing particle size. The V content is due to the high V supplementary fuel. The Mn and Mo are probably from local water used in the process. Good agreement was obtained for Na, Cl, S, and K between the two different recovery boilers.

Table 7 presents the results for emissions from the power boiler of the pulp and paper mill. This boiler burns bark and scrap wood chips with fuel oil as a supplemental fuel. As expected, the Fe, Ca, K, Mg, Cl, Si, and Ti content decreased with decreasing particle size. The Sn, S, Cl, Mn, Sr, Mo, and K are found even in the smallest particles.

Summary

The results of the elemental content of sized emissions from different industries are presented. These data were obtained from the samples collected with standard in-stack impactors, series cyclones, a diffusional device, and a special XRF-compatible impactor. The samples collected with the standard in-stack impactors and cyclones had to be transferred to a suitable substrate for XRF analyses while the other two collectors produced samples that were analyzed by x-ray as received. Most of the results were as expected. The exceptions are the high Fe in the very small ($<0.03 \mu\text{m}$) particles and the uniform distribution of the S in the oil-fired power plant emissions.

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Disclaimer

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Table 1
EPA Multispectrometer XRF Analyzer Element Sensitivities and Detection Limits

Element	Sensitivity counts/100 sec $\mu\text{g}/\text{cm}^2$	Detection ^a limit (100 sec, 3 σ) ng/cm^2	Element	Sensitivity counts/100 sec $\mu\text{g}/\text{cm}^2$	Detection ^a limit (100 sec, 3 σ) ng/cm^2
F	220	149	Co	16540	3
Na	534	29	Ni	14504	10
Mg	10280	2	Cu	18880	43
Al	8074	3	Zn	21066	7
Si	11614	3	As	17125	10
P	13392	15	Se	22922	12
S	28013	9	Br	50340	28
Cl	25394	9	Cd	17303	2
K	121286	2	Sn	14800	2
Ca	87817	2	Sb	31100	4
Ti	85635	2	Ba	25000	7
V	18010	7	Pt	6812	20
Cr	7484	19	Au	8498	91
Mn	17522	14	Hg	5776	90
Fe	13300	18	Pb	16583	30

^aDetermined on 3.8 μ Mylar substrate using chromium tube at 50 kV, 50 mamp

Table 2
Distribution of Important Elements
in Sized Fractions Oil-Fired Power Plant

Stage D ₅₀ μm	Elements, weight percent						
	S	V	Ni	Fe	Ca	Si	Al
23.0	5.3	2.8	0.3	2.7	0.4	0.2	0.1
10.0	3.6	2.0	0.2	1.4	0.1	0.3	0.03
4.7	1.9	0.4	0.03	0.2	0.05	0.6	0.009
1.9	4.6	0.6	0.02	0.2	0.04	0.6	0.008
1.0	3.5	0.5	0.03	0.3	0.1	0.3	0.02
0.52	4.9	0.3	0.02	0.2	0.02	0.6	NF
0.27	2.4	0.007	NF	0.02	0.009	0.1	NF
Filter	1.7	5.1	0.8	0.1	NF	NF	NF

Table 3
Distribution of Elements on Stages of Three Series Cyclone System
Oil-Fired Power Plant

Stage	Cutpoint μm	Percent of Total on Each Stage						
		Total Mass	Sulfur			Vanadium		Nickel
		Excess Oxygen	0.2	1.0	0.2	1.0	0.2	1.0
Cyclone 1	3.3	80.2	1.1	81.4	3.2	45.9	3.6	47.6
2	1.8	2.2	0.0	3.4	0.5	2.5	0.7	2.1
3	0.8	0.2	0.1	0.2	0.5	0.5	0.6	0.4
Filter		17.4	98.8	15.0	95.8	51.1	95.1	49.9
								96.4

Table 4
Diffusion Classifier Runs, Coal-Fired Power Plant¹
Concentration in μg

Diameter μm	<0.03	0.03 - 0.07	0.07 - 0.12	0.12 - 0.3	>0.3
Mg	-- ²	--	--	0.7	0.068
Al	--	0.1	0.13	0.13	0.19
Si	0.24	0.24	0.20	0.21	0.54
Ca	0.4	0.33	0.25	0.2	0.34
Fe	23.9	4.1	11.5	11	30

¹ Average of six 60 minute runs

² None detected

Table 5
XRF Impactor Data for Pulp and Paper Mill
Concentration μg *

D_{50} in μm	Precutter 15	8	4	2	1	0.5
Na	41.5	26.5	22.5	30.5	100	86
S	152	114	69	53	170	142
Cl	20.5	19.5	8.9	5	13.5	42
K	40	31.5	17.5	11.3	37.5	49

* Average of two runs

Table 6
XRF Impactor Results from Recovery Boiler
Pulp and Paper Plant
Concentration in μg

D_{50} in μm	15 (Precutter)	8	6	4	1	0.5
Na	44	49	28	27	146	180
S	97	103	48	33	198	223
Cl	12	14	9	9	27	43
K	22	25	11	7	41	54
V	D ¹	0.5	0.4	D	D	0.4
Mn	15	16	16	15	12	15
Br	1.5	2.2	1.7	1.3	0.9	2.5
Sr	7	8	8	7	4	8
Mo	12	13	12	11	D	13
Cd	0.02	0.06	--	D	0.5	0.03
Sn	2	2	2	1.6	1.9	2

¹ Detected but below 3σ of background

Table 7
XRF Impactor Data for Pulp and Paper
Mill Power Boiler
Concentration μg

D ₅₀ in μm	15 (Precutter)	8	6	4	1	0.5
Mg	23	14	8.6	3	1.0	D
Al	26	14	9.3	2.6	0.9	NF
Si	40	18	10	2.	0.8	NF
S	42	21	14	5.9	4.1	3.1
Cl	8	12	6.8	2.6	2.5	1.1
K	57	39	26	11	9.3	6.9
Ca	173	46	22	NF	NF	NF
Ti	1.8	1.2	0.9	0.4	0.4	D
Mn	3.5	8.4	8.0	7.5	6.3	5.7
Fe	260	5	3.4	1.0	NF	NF
Br	NF	1.5	NF	0.7	0.4	D
Sr	4.7	9.7	7.3	8.1	7.3	6.0
Mo	5.6	15	10	11	11.7	9.1
Sn	1.9	2.6	2.1	1.3	2.0	1.0
Ba	1.9	1	0.6	D	D	NF

NF - None found

D - Detected but below 3σ